Direct synthesis of vertical α-Fe_2O_3 nanowires from sputtered Fe thin film

Keisuke Nagato,[a] Masaki Furubayashi, Tetsuya Hamaguchi, and Masayuki Nakao
Department of Mechanical Engineering, Graduate School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

(Received 7 July 2010; accepted 20 September 2010; published 28 October 2010)

α-Fe_2O_3 (hematite) nanowires were synthesized from Fe thin films. The bladelike nanowires were synthesized by the simple annealing of a sputtered Fe thin film in a furnace with the annealing time varied between 0 and 100 min. The length of the nanowires was proportional to the logarithm of the annealing time. The number density of nanowires was saturated within an annealing time of 0–1 min. The Fe thin film may have been oxidized during annealing and the iron oxide molecules may have diffused to the roots of nanowires in accordance with the solid-phase growth model or they may have vaporized and then have been deposited on the surface of nanowires in accordance with the vapor-liquid-solid model. The authors characterized the nanowires by Raman spectroscopy and transmission electron microscopy (TEM). The Raman shift and the results of TEM indicated that the nanowires consisted of trigonal α-Fe_2O_3. © *2010 American Vacuum Society.*
[DOI: 10.1116/1.3501363]

I. INTRODUCTION

Iron oxide nanowires have interesting electrical, chemical, and magnetic properties, and are potentially applicable to various nanodevices such as field-emission devices,[1,2] gas sensors,[3–5] field effect transistors,[6] magnetic recording,[7] and electrodes for lithium ion batteries.[3] Generally, iron oxide nanowires can be synthesized by the simple annealing of Fe. In some studies, the nanowires have been synthesized from bulk Fe substrates,[7,8] and their field-emission properties and magnetic properties and the effect of changing their electrical resistance by gas contamination have been investigated. However, there have been no reports on whether deposited Fe can be used as a seed layer for the synthesis of nanowires or on the time dependence of nanowire growth, such as the growth rate of length or number density. If iron oxide nanowires can be directly synthesized from a deposited seed layer, then they can be more easily integrated into nanodevices. When the seed layer is patterned, the position of nanowires can be controlled. For example, for integration of gas sensors[9] or surround-gate field effect transistors,[10] it is suitable that the nanowires are synthesized over a base electrode or circuit substrates.

Furthermore, because the seed layer is expected to be reproducible from the viewpoints of oxidation degree, crystallinity, flatness, and thickness, the synthesis of nanowires will be controllable. In this article, we investigated the growth of nanowires from a sputtered Fe thin film. The growth rate was investigated using scanning electron microscopy (SEM) observation, Raman spectroscopy, and transmission electron microscopy (TEM).

II. EXPERIMENT

The synthesis procedure is as follows. Fe and Cr thin films were deposited on a Si substrate with thicknesses of 200 and 50 nm, respectively, by rf magnetron sputtering. The base pressure and sputtering pressure (Ar) were 4×10^{-4} and 5×10^{-3} Pa, respectively. The Cr thin film was deposited to avoid the detachment of the Fe film from the substrate. The substrate was placed in a furnace with an air flow of 2.5 l/min. The pressure of the furnace was maintained at 0.1 MPa, i.e., atmospheric pressure. The sample was heated to 375 °C in 1 min then this temperature was maintained for 0–100 min. The furnace was then cooled to room temperature in about 30 min. We also investigated the synthesis of nanowires on Si (100) substrates patterned by KOH anisotropic etching. We deposited the Fe/Cr thin films onto these substrates and annealed them under the same conditions as those for the flat substrates.

The synthesized nanowires were observed by SEM and the growth rate was investigated. Raman spectroscopy was used to characterize the time dependence of the crystallinity of the substrate and nanowires. Using TEM, crystalline characteristics such as lattice clearance and direction were revealed.

III. RESULTS AND DISCUSSION

Figure 1 shows the SEM images of the initial film (a) and the synthesized nanowires [annealing times: 0/1/3/10/30 min (b)–(f)]. Vertical bladelike or wirelike nanostructures with sharp apexes and a greater width at the base were synthesized on the substrate. As the annealing time increased, the nanowires became longer and wider. Figure 2 shows the length and density of the nanowires as a function of the logarithm of annealing time. Note that we plotted the data for 0 min at 0.5 min because the sample was not heated and cooled instantaneously in the furnace. The number density was saturated within 0–1 min of annealing. The nanowire length was proportional to the logarithm of the annealing time between 0.5 and 20 min. The length of nanowires became saturated after about 20–30 min. The length of nanowires synthesized with an annealing time of 100 min was

[a]Electronic mail: nagato@hnl.t.u-tokyo.ac.jp

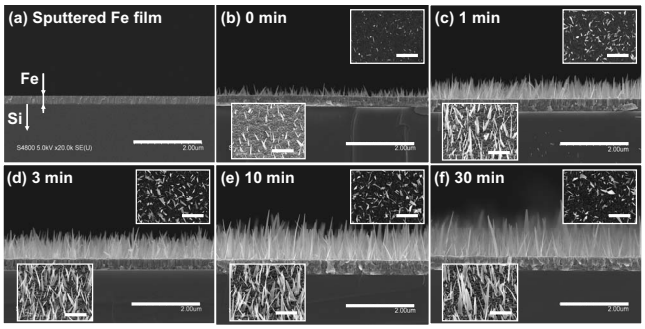

FIG. 1. Cross-sectional SEM images of the Fe thin film (a) and synthesized iron oxide nanowires with annealing times of 0 (b), 1 (c), 3 (d), 10 (e), and 30 min (f). The insets show top and tilted images (45°). All the scale bars indicate 2 μm.

comparable to those grown for 20 and 30 min. According to the cross-sectional SEM images shown in Fig. 1, the initial Fe film was 200 nm in thickness; however, the thickness increased to 400 nm in the samples annealed for 20, 30, and 100 min. Generally, the synthesis of metal oxide nanowires grown by the oxidation of a metal substrate is considered to follow the vapor-liquid-solid growth model[11] or the solid-phase growth model.[12] In these models, the Fe atoms initially enter the liquid phase and are then oxidized, and the FeOx nanowires grow at the boundary between the liquid Fe and the oxidized Fe (solid). While the nanowires grow, the oxidation of the Fe film proceeds. Therefore, the nanowire growth may stop when the Fe film is completely oxidized.

Figure 3(a) shows the Raman spectra of the nanowires grown with annealing times of 0/1/3/10/30 min. The intensity of Fe_2O_3 increased with the annealing time. Intriguingly, the samples with annealing times of 0 and 1 min have peaks

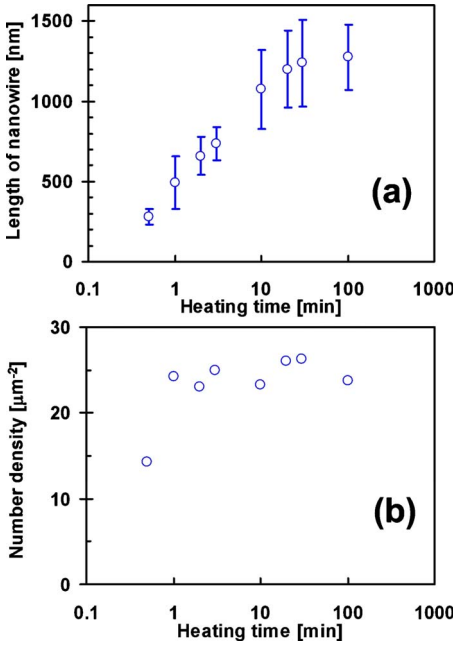

FIG. 2. (Color online) (a) Average length and (b) number density of nanowires as a function of logarithm of annealing time.

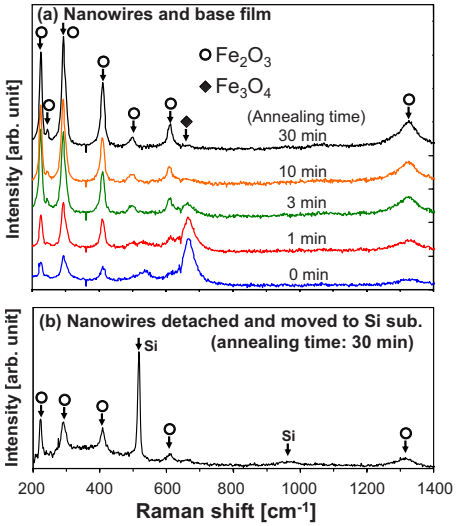

FIG. 3. (Color online) Raman spectra of (a) the nanowire substrates annealed for 0/1/3/10/30 min and (b) nanowires which was removed from the substrate onto a Si substrate.

corresponding to Fe_3O_4.[13,14] Fe_3O_4 is called magnetite and is an intermediate product formed synthesis the Fe_2O_3. Figure 3(b) shows the nanowires which are detached from the base film and moved onto a Si substrate. The peaks due to Fe_2O_3 are obtained with those of Si. All the nanowires synthesized with annealing time of 0/1/3/10/30 min were Fe_2O_3. Thus, the Fe_3O_4 observed from the samples with the annealing time of 0/1/3 min were due to oxidized Fe film.

The nanowires were observed by TEM (Fig. 4). A nanowire was removed from the sample with an annealing time of 30 min. Lattices were observed in TEM images and the electron diffraction pattern (EDP) was observed. According to Ref. 15, the EDP is that of trigonal Fe_2O_3. A single- or polycrystal structure was observed throughout the nanowires.

To investigate the effect of the surface on the growth direction, we synthesized nanowires from an Fe thin film that had been sputtered on a patterned substrate. Figure 5 shows the results. The nanowires were synthesized with a regular vertical alignment on the surface. We consider that nucleation occurred in a certain crystal direction at the boundary

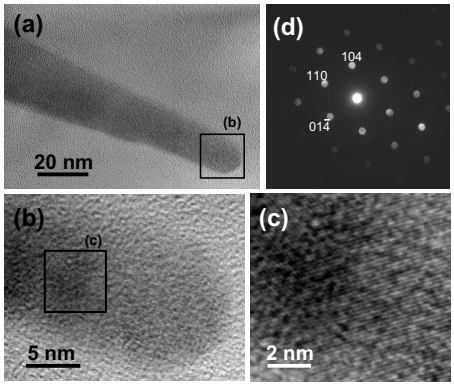

FIG. 4. TEM images of a nanowire. (a) Low-magnification image, [(b) and (c)] high-magnification images, and (d) diffraction pattern.

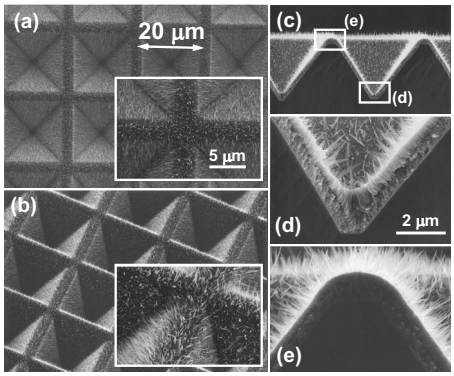

FIG. 5. SEM images of nanowires synthesized from a patterned substrate (20 μm pitch pyramidal holes). (a) Top images, (b) tilted images (45°), and [(c)–(e)] cross-section images. The annealing time was 30 min.

between the liquid Fe and the oxidized Fe crystal and the nanowires grew vertically in this direction. To clarify the growth mechanism, further investigation, such as the observation of the boundary between the film and the nanowire, is needed.

IV. CONCLUSIONS

We investigated α-Fe_2O_3 nanowires synthesized from sputtered Fe thin films. For the synthesis, a flow of air at atmospheric pressure, an annealing temperature of about 375 °C, and an annealing time of 0–100 min were required. It was found that nanowires with a length from approximately 200 nm to over 1 μm grew from an Fe film with a thickness of 200 nm when the annealing time was 0–100 min. Furthermore, we discovered that the nanowires grew vertically on the surface. Using a deposited Fe thin film as a seed layer, the device integration of nanowires is expected to be more easily, controllably, and reproducibly achieved.

ACKNOWLEDGMENTS

The patterned Si substrate was fabricated using the EB writer (F5112+VD01) at the University of Tokyo VDSI Design and Education Center (VDEC), which was donated by Advantest Corporation. This work was partially supported by Grant-in-Aid for Scientific Research (Grant Nos. 19106003 and 21860015) and by the Global Center of Excellence (G-COE) Program "Global Center of Excellence for Mechanical Systems Innovation (GMSI)" from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

[1]Y. W. Zhu, T. Yu, C.-H. Sow, Y. J. Liu, A. T. S. Wee, X. J. Xu, C. T. Lim, and J. T. L. Thong, Appl. Phys. Lett. **87**, 023103 (2005).
[2]T. Yu, Y. Zhu, X. J. Xu, K.-S. Yeong, Z. Shen, P. Chen, C.-T. Lim, J. T.-L. Thong, and C.-H. Sow, Small **2**, 80 (2006).
[3]J. Chen, L. Xu, W. Li, and X. Gou, Adv. Mater. **17**, 582 (2005).
[4]Z. Sun, H. Yuan, Z. Liu, B. Han, and X. Zhang, Adv. Mater. **17**, 2993 (2005).
[5]G. Wang, X. Gou, J. Horvat, and J. Park, J. Phys. Chem. C **112**, 15220 (2008).
[6]Z. Fan, X. Wen, S. Yang, and J. G. Lu, Appl. Phys. Lett. **87**, 013113 (2005).
[7]C. H. Kim *et al.*, Appl. Phys. Lett. **89**, 223103 (2006).
[8]S. Rackauskas *et al.*, Nanotechnology **20**, 165603 (2009).
[9]S. O. Hwang, C. H. Kim, Y. Myung, S.-H. Park, J. Park, J. Kim, C.-S. Han, and J.-Y. Kim, J. Phys. Chem. C **112**, 13911 (2008).
[10]P. Nguyen, H. T. Ng, T. Yamada, M. K. Smith, J. LI, J. Han, and M. Meyyappan, Nano Lett. **4**, 651 (2004).
[11]Y. Q. Zhu, W. Hu, W. K. Hsu, M. Terrones, N. Grobert, J. P. Hare, H. W. Kroto, D. R. M. Walton, and H. Terrones, Chem. Phys. Lett. **309**, 327 (1999).
[12]Y. Kojima, K. Kasuya, K. Nagato, T. Hamaguchi, and M. Nakao, J. Vac. Sci. Technol. B **26**, 1942 (2008).
[13]D. L. A. de Faria, S. V. Silva, and M. T. de Oliveira, J. Raman Spectrosc. **28**, 873 (1997).
[14]D. L. A. de Faria and F. N. Lopes, Vib. Spectrosc. **45**, 117 (2007).
[15]JCPDS Card No. 33-0664.